XL.—*The Influence of Temperature on the Interaction between Acetyl Thiocyanate and Certain Bases. Thiocarbamides, including Carboxy-aromatic Groups.*

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Introduction [by the Compiler].

As the result of investigations which have now been carried on for several years in the chemical laboratory of Queen's College, Cork, a considerable body of evidence has been accumulated, going to establish amongst certain acyl thiocyanates the existence of a peculiar kind of tautomerism, which is characterised by the power exhibited by these substances of behaving either as such or as thiocarbimides, according to the conditions under which they are caused to interact (Trans., 1904, 85, 807). Until comparatively recently, it had not been suspected that temperature alone might be a determining factor in these tautomeric phenomena; for although it is well known to effect the change of unsaturated hydrocarbon thiocyanates into the isomeric

thiocarbimides, no such permanent change has yet been observed in the case of thiocyanates of distinctly acidic radicles.

The discovery that Miquel's "acetyl thiocyanate" (*Ann. Chim. Phys.*, 1877, [v], 11, 295), when interacting with aniline, behaves at high temperatures principally as thiocarbimide, whilst at low temperatures it exchanges to a large extent the thiocarbimidic character for that of a thiocyanate, occurred fortuitously during the course of some experiments made in order to determine the capacity possessed by certain acidic groups of expelling others from combination. Acetylphenylthiocarbamide being required in connection with this work, its preparation was conducted by mixing at the ordinary temperature of the laboratory benzene solutions of acetyl thiocyanate (prepared from acetyl chloride and lead thiocyanate) and aniline. Forty per cent. only was obtained of the theoretical yield, reckoned from the weight of acetyl chloride employed, and calculated on the basis of the equations:

1. $2\text{CH}_3\cdot\text{COCl} + \text{Pb}(\text{SCN})_2 = \text{PbCl}_2 + 2\text{CH}_3\cdot\text{CO}\cdot\text{NCS}$.
2. $\text{CH}_3\cdot\text{CO}\cdot\text{NCS} + \text{C}_6\text{H}_5\cdot\text{NH}_2 = \text{CH}_3\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$.

A similar result followed on repeating the process, and since acetyl thiocyanate is somewhat prone to decomposition, during another experiment the reagents were surrounded by running cold water. However, the effect of this precaution was that a smaller yield was obtained than when it was not taken.

Again the experiment was tried, with constituents heated beforehand to 40° ; a much better yield was now produced, which was improved still further by mixing the solutions at temperatures near their respective boiling points, the combination in these circumstances being somewhat violent.

Following up these results, an inquiry was commenced for the purpose of determining quantitatively the course of the interaction at different temperatures, and the general conclusions were summarised in a brief preliminary note (*Proc.*, 1904, 20, 20). The intention was to refrain from fuller publication until sufficient data should be available to permit of the graphic plotting of the results; but unhappily the progress of this research has been interrupted by Mr. Doran's untimely death.

His note-book, containing the record of a number of experiments on this subject, together with a few hitherto unpublished observations in connection with his work on the chlorocarbonates (*Trans.*, 1896, 69, 324; 1901, 79, 906), has been handed to me for compilation, in order that the scientific results might be preserved, for, unfortunately, these had not been incorporated in the form of a paper. In the present communication, therefore, the experimental data are the author's; for the rest, the compiler alone is responsible. (A. E. D.)

Part I.

Acetyl Thiocyanate and Aniline.

Except in a few cases, specifically mentioned below, the general method of procedure, when working at low or moderate temperatures, was as follows: a weighed quantity of acetyl chloride, dissolved in anhydrous benzene, was heated with excess of dry lead thiocyanate until the solution ceased to give the reactions of chlorine. After separating the insoluble lead salts at the pump, the liquor was treated with aniline, dissolved in benzene, and added from a burette until two molecular proportions of base were present for each molecular proportion of acetyl chloride taken, or until the odour of acetyl thiocyanate was no longer perceptible. After a short time, the benzene mother liquor was poured off from the precipitate, and the solution allowed to evaporate at the temperature of the air; the solid residue of this evaporation was variable in amount, and consisted principally of acetylphenylthiocarbamide. In the precipitate, which was sometimes oily and sometimes granular, aniline thiocyanate and acetanilide were found, together with more or less acetylphenylthiocarbamide. When operating at temperatures higher than 20° , the constituents were heated separately to the initial temperature of the experiment and then mixed; where it was desired to work at the highest temperatures attainable in open vessels, with benzene or toluene as solvent, one constituent was boiled in a reflux apparatus, while the other was allowed to drip in slowly from a tap-funnel; in such preparations, only one molecular proportion of base was employed for each molecular proportion of acetyl chloride taken, a further charge being added subsequently to the warm mixture if any odour of thiocyanate could be detected. Usually, in these cases, little or no precipitate appeared until the solutions were concentrated by spontaneous evaporation at the ordinary temperature; it may here be mentioned incidentally, that if a mixture of aniline thiocyanate with much benzene is heated on the water-bath sufficiently to drive off all the benzene, isomeric change into phenylthiourea occurs to a very perceptible extent.

Without going into details concerning the results of individual experiments, the conclusions to which they lead may be stated, qualitatively and quantitatively, so far as these experiments have been carried, in the following way.

Acetyl thiocyanate, when interacting with aniline, produces always more or less acetylphenylthiocarbamide, and hence does not act exclusively as thiocyanate; neither does it behave purely as a thiocarbamide, for the products have never yet been found quite free from aniline thiocyanate. Two processes, in fact, appear to take place simultaneously:

(i) An additive-compound is formed, thus :

(ii) Double decomposition occurs, according to the equations :

If the temperature of interaction is kept very low, process (i) is almost in abeyance, the action occurring as in (ii), but with rising temperature this kind of change becomes less and less marked, until, in boiling benzene, over nine-tenths of the weight of acetyl compound present unites additively with the aniline, as shown by equation (i), to form the disubstituted thiocarbamide.

Of the three products, namely, aniline thiocyanate, acetanilide, and acetylphenylthiocarbamide, the first is nearly insoluble in benzene, the second is but sparingly soluble in the cold, the third dissolves to a moderate extent ; in those cases where aniline caused direct precipitation, the benzene mother liquor was evaporated to dryness and the residue, if trifling, accounted as thiocarbamide ; but if it amounted to several grams, the acetanilide was removed by crystallising from dilute alcohol, in which the thiocarbimide is but sparingly soluble at the ordinary temperature. To separate the constituents of the precipitate which formed in the benzene solution when aniline was added, the dry mixture was treated with cold water until free from aniline thiocyanate ; the aqueous extract, when evaporated to dryness, left a residue, which was weighed and considered to be the aniline thiocyanate originally present. In some experiments, the residue left after extraction of the aniline thiocyanate was dried and weighed again, the difference between the two weighings being taken as a measure of the aniline thiocyanate. Finally, the residue was dissolved in boiling dilute alcohol, from which, on cooling, most of the thiocarbamide crystallised out, and was weighed directly ; the acetanilide was determined, sometimes by difference and sometimes by evaporating to a small bulk the weak alcoholic solution from which the thiocarbamide had been deposited, and collecting the anilide which separated out, the latter method being preferred, since, by determining the melting point of the product, it could be ascertained whether the anilide was tolerably pure.

It need scarcely be said that the methods employed, especially those for the quantitative determination of the products, are capable of yielding only very rough approximations to the actual values, more particularly as regards the proportion of acetylphenylthiocarbamide, a value which it was important to secure. But the investigation, so far as it had gone, amounted to little more than a series of preliminary

experiments, in which no greater accuracy was contemplated than would suffice to indicate broadly the course of the interactions. In such a series, no special precautions were taken to secure uniformity; the acetyl chloride was used as purchased, and contained phosphorus, the aniline was not freshly distilled, variable weights of materials were employed for interaction, and the degree of dilution of the materials with benzene was not measured. Naturally, therefore, the results present certain discrepancies in detail, but not such as to obscure the main issue.

The following experiments are arranged, not in the order of their performance, but according to the temperatures at which the constituents were mixed. Moreover, the quantities of acetyl thiocyanate named are calculated (save where the pure substance was employed) from the weight of acetyl chloride taken, assuming a quantitative exchange of chlorine for the thiocyanogen group.

No. 1.—Temperature of interaction from -8° to -3° : 5.05 grams of pure freshly distilled acetyl thiocyanate and 9.3 grams of aniline yielded 13.5 grams of solid matter; the mother liquor, free from thiocyanic acid, gave 0.5 gram of acetylphenylthiocarbamide, the total weight being 14 grams. The precipitate, which appeared to consist entirely of acetanilide and aniline thiocyanate, gave on treatment with water 6 grams of acetanilide, against 6.45 calculated, after allowing for the amount of thiocarbamide obtained; this leaves 7.5 for the aniline thiocyanate, but on evaporating the solution only 5 grams of solid were left. The weight of acetylphenylthiocarbamide corresponds to 5.2 per cent. of what the acetyl compound could yield if acting exclusively as thiocarbimide.

No. 2.—Temperature, -5° to -2° : 5.05 grams of acetyl thiocyanate in much benzene and 9.3 grams of aniline yielded very little solid, the product being mainly oil. In all, 9.7 grams were obtained, together with 1.5 grams from the mother liquor, the whole containing 1.3 grams of acetylphenylthiocarbamide (m. p. $171-172^{\circ}$). The 9.7 grams of precipitate were resolved by cold water into 4.5 grams of residue, whilst 4.5 grams were left on evaporating the aqueous extract; 0.7 gram, therefore, remains unaccounted for in this process. Acetylphenylthiocarbamide (1.3 grams) would absorb 0.675 gram of acetyl thiocyanate, leaving 4.325 grams to behave as acetylthiocarbimide; this should give 12.3 grams of mixture, whereas 9.7 grams only were obtained. Assuming this mixture to consist solely of thiocyanate and anilide, the latter would amount to about 4.56 grams, whilst, as stated above, 4.5 grams of crude acetanilide were left. The weight of acetylphenylthiocarbamide produced corresponds to about 13.5 per cent. of what could result if the yield of the acetyl compound were quantitative and its function purely thiocarbimide (this is called below the

"possible yield"), and the total weight of products accounts for 81 per cent. of the acetyl chloride used.

No. 3.—Temperature, -6° to $+1^{\circ}$ (mean about -2°): 10.1 grams of acetylthiocyanate and 18.6 grams of aniline yielded 20 grams of solid matter, and 3 grams of acetylphenylthiocarbamide were found in the mother liquor. When extracted with cold water, the main crop left 7 grams of acetanilide not quite free from thiocarbamide, and the extract gave 13 grams of residue, mostly aniline thiocyanate. This salt cannot be evaporated to dryness in aqueous solution without undergoing some change into phenylthiourea. Reckoned as in the preceding experiment, the yield of acetylphenylthiocarbamide amounts to about 15.5 per cent. of that possible, and the total weight of products accounts for some 85 per cent. of the acetyl chloride employed.

No. 4.—Temperature, 20° , rising to 55° (mean about 37°): 5.05 grams of acetylthiocyanate and 7.65 grams of aniline gave 3.2 grams of acetylphenylthiocarbamide, or about 33 per cent. of the possible yield; in addition, there were 2 grams of acetanilide and 2.5 grams of aniline thiocyanate. These products would absorb in their formation 1.66 grams of acetyl thiocyanate and 0.75 and 0.83 gram respectively of acetylthiocarbimide, the total, 3.24 grams, corresponding to 68 per cent. of the acetyl chloride taken.

No. 5.—Temperature, 40° to 50° (mean about 45°): 10.1 grams of acetyl thiocyanate and 14.3 grams of aniline yielded 9 grams of acetylphenylthiocarbamide, corresponding to 46.5 per cent. of the possible yield, and absorbing 4.68 grams of acetylthiocarbimide; in addition, there were 13 grams of mixed anilide and thiocyanate, thereby accounting for 92 per cent. of the acetyl chloride used.

No. 6.—Temperature, 50° to 85° (mean about 67°): 5.05 grams of acetyl thiocyanate and 5.65 grams of aniline. On bringing the constituents together, the temperature rose quickly to 85° , whereupon the mixture began to boil. A solid mixture (10.5 grams) was obtained, which gave up to cold water 2.5 grams of aniline thiocyanate; the remaining 8 grams were resolved into 4 grams of pure recrystallised acetylphenylthiocarbamide and 2 grams of acetanilide. Since the 2.5 grams of thiocyanate would be accompanied by 2.8 grams of acetanilide, the 4 grams of recrystallised thiocarbamide came, presumably, from 5.2 grams originally present in the mixture. That is, 53.5 per cent. of the acetyl compound, supposing it to be formed quantitatively, has acted as thiocarbimide; the remainder, acting as thiocyanate, should give 6.65 grams of mixed anilide and thiocyanate, or a total of 11.85 grams against the 10.5 grams obtained. Hence, in this experiment, of the acetyl chloride employed, about 89 per cent. is accounted for.

No. 7.—10.1 grams of acetyl thiocyanate and 9.3 grams of aniline, both dissolved in benzene, were heated separately to 75° and the solutions mixed in bulk; the mixture boiled freely, but nothing separated, except a trace of oily matter. The solution, when poured off from this and left, slowly deposited 10 grams of practically pure acetylphenylthiocarbamide (m. p. 171—172°); the mother liquor required 3 grams more of aniline to destroy the odour of acetyl thiocyanate, and by evaporation gave 8.5 grams of a solid containing very little thiocarbamide, but giving distinctly the reactions of aniline thiocyanate. The yield of acetylphenylthiocarbamide amounts to 41.5 per cent. of that possible, whilst 77.5 per cent. of the acetyl chloride taken is accounted for in the total weight of products obtained.

The three following experiments were conducted by allowing the acetyl compound to drip slowly down a tube, passing through a vertical condenser into a boiling solution of the amine, or *vice versa*; the temperatures were not measured, but where benzene was employed as solvent were probably not very far from 85°.

No. 8.—10.1 grams of acetyl thiocyanate in benzene were passed slowly into a boiling solution of 9.3 grams of aniline in benzene; on cooling, 11 grams of thiocarbamide crystallised out, and the mother liquor, when concentrated, gave 6 grams more of the same substance, the total amounting to about 88 per cent. of the possible yield.

No. 9.—The preceding experiment was repeated under identical conditions, except that the amine was dropped into the solution of the thiocyanate and the mixture effected more rapidly: 15.5 grams of acetylphenylthiocarbamide resulted, or about 80 per cent. of the possible yield; in both this and the preceding experiment, the mother liquor gave marked indications of thiocyanic acid.

No. 10.—5.05 grams of acetyl thiocyanate were used, the solution of the amine (4.65 grams) being admitted below the surface of the boiling liquid; in this way, 8.8 grams of thiocarbamide were obtained, or about 91 per cent. of the possible quantity.

No. 11.—5.05 grams of pure distilled thiocyanate and 4.7 grams of aniline, each dissolved separately in boiling toluene, were mixed quickly; the interaction was very vigorous, and ultimately 8 grams of acetylphenylthiocarbamide were collected, amounting to only 82.5 per cent. of the possible yield. The mother liquor reacted very freely for thiocyanic acid.

In certain of the experiments described above, the change of temperature during the interaction was so large compared with the total range brought under observation that it is difficult to connect yield and temperature save in an approximate manner, which does not admit of the results being plotted as a curve. Moreover, even if the

temperatures were known within a few degrees for each interaction, it is doubtful whether the methods adopted for measuring the yields of the various products are sufficiently precise to define its shape. Nevertheless, it is easy enough to follow in a general way the effect produced by increasing temperature on the power exhibited by acetyl thiocyanate of affording a thiocarbamide with aniline; unfortunately, the determinations of the relative quantity of thiocyanic acid formed, also an important factor, are too few and too erratic to lend themselves to tabulation.

As a basis for the figures given in the following table, the method of calculation adopted is this: (i) where the temperature varied much during interaction, the mean value is taken; in cases where boiling occurred, the temperature thereby attained is taken as 85° ; (ii) it is assumed that the whole of the acetyl chloride employed in any experiment is converted into the corresponding thiocyanate, and that the latter is collected without loss; (iii) the weight of acetylphenylthiocarbamide obtained is taken as the measure of the quantity of acetylthiocarbimide present at a given temperature, the percentage of acetylthiocarbimide being calculated on the principle that a yield of 194 parts of thiocarbamide for 78.5 parts of acetyl chloride employed would correspond to 100 per cent. of acetylthiocarbimide existing in the "thiocyanate." Experiments 9 and 11 have not been incorporated in the table, the former being omitted because the usual order of mixing the constituents was reversed, and the latter because a different solvent was employed.

Table showing the Effect of Temperature on the Interaction between Aniline and Acetyl Thiocyanate.

No. of experiment.	Mean temperature of interaction.	Percentage of acetyl thiocarbimide.	No. of experiment.	Mean temperature of interaction.	Percentage of acetyl thiocarbimide.
1	-5°	5.2	6	$+67^{\circ}$	53.7
2	-4	13.4	7	$+80 (?)$	51.5
3	-2	15.5	8	{ B.p. of benz. } { ene solution }	87.7
4	$+37$	33.0	10		91.0
5	$+45$	46.5			

Acetyl Thiocyanate and other Bases.

(a) o-Toluidine.

Two experiments were carried out in benzene solution.

(i) 5.05 grams of acetyl thiocyanate were added slowly to 10.7 grams of *o*-toluidine at about -3° . Solid and oil were formed, the latter being separated as far as possible at the pump; the residue, a sticky mass weighing 9 grams, when recrystallised from spirit, gave 6 grams of acetyl-*o*-tolylthiocarbamide, melting at $183-184^{\circ}$.

(ii) This process was repeated at the boiling point with 5.05 grams of acetyl thiocyanate and 5.5 grams of amine; 9.5 grams of crystalline solid resulted, and the mother liquor gave 0.3 gram more, together with some oily droplets, reacting strongly for thiocyanic acid. On recrystallisation, the main crop gave 8.5 grams of acetyl-*o*-tolylthiocarbamide (m. p. 184°).

So far as can be judged from these experiments, temperature has little influence, if any, between the limits indicated, on the combination between *o*-toluidine and acetylthiocarbamide, the yields of additive product amounting respectively to 86.5 and more than 91 per cent. of that theoretically possible; the slight deficiency in the former case may perhaps be due to the solvent action of a quantity of uncombined *o*-toluidine.

(b) *Secondary Bases.*

(i) *Methylaniline.*—Concurrently with the foregoing experiments, attempts were made to combine acetyl thiocyanate with some secondary bases; the first of these selected was methylaniline. Vigorous interaction occurred on mixing the constituents in benzene solution, heated nearly to the boiling point; the mixture on cooling deposited white crystals amounting to about 36 per cent. of the possible yield. When recrystallised from dilute alcohol, the product melted at 93–94° with decomposition, and afforded 15.56 per cent. of sulphur against 15.4 calculated for $C_{10}H_{12}ON_2S$. Acetylmethylphenylthiourea dissolves very freely in alcohol and in benzene, and is desulphurised by alkaline lead solution only after prolonged boiling.

(ii) *Benzylaniline.*—Combination was less energetic than in the preceding case, but the yield was very satisfactory, amounting to more than 91 per cent. of that theoretically possible. When recrystallised from weak spirit, the substance formed a mass of fine rhombic crystals melting at 110–111°.

Found, S = 11.23; $C_{16}H_{16}ON_2S$ requires S = 11.26 per cent.

Acetylphenylbenzylthiourea is readily soluble in hot alcohol or benzene, moderately so in cold; it is insoluble in water, and nearly insoluble in light petroleum.

(iii) *Piperidine.*—With this base, somewhat singular results were obtained, of which a satisfactory explanation is still wanting.

Piperidine (8.5 grams), dissolved in benzene, was dropped slowly into a boiling benzene solution of 10.1 grams of acetyl thiocyanate; very vigorous action occurred, and even while the liquid was still hot a solid separated in large, shining plates. On cooling, this product was collected; its weight amounted to 2 grams, and the substance, when recrystallised from chloroform, melted at 95–96° and proved

to be piperidine thiocyanate. The mother liquor reacted strongly for thiocyanic acid, and was freely desulphurised by alkaline lead or silver salts, but no sign of solid matter was observed in the viscid residue, even after very prolonged standing. After several months, the residue was mixed with alcohol, whereupon the odour of ethyl acetate soon became distinctly perceptible, increasing gradually to a maximum and then slowly passing off; meanwhile, very fine large crystals began to be deposited, of which, after a few weeks, two grams were obtained; they melted, both before and after recrystallisation, from a mixture of alcohol with benzene at 126—127°, but proved not to be the expected acetylpiiperidylthiourea.

The product exhibited the general properties of a thiourea, being readily desulphurised, for instance, by ammoniacal silver nitrate even in the cold; but an analysis gave $S=22.1$, whilst the compound $\text{AcN}\cdot\text{C}(\text{SH})\cdot\text{NC}_5\text{H}_{10}$ would require $S=17.21$ per cent. But the properties, the melting point, and the amount of contained sulphur are all consistent with the view that the substance is identical with the "piperidylthiourea" obtained by Wallach (*Ber.*, 1899, 32, 1872) from cyanogen bromide, piperidine, and hydrogen sulphide. The experiment was twice repeated with precisely similar results; in one case, every precaution was taken against access of moisture and a slightly increased quantity of the amine was used; no difference whatever was observed in the course of the process, but ultimately larger yields of piperidine thiocyanate and the thiourea were obtained, amounting to 3.2 grams of the former and 4.0 grams of the latter, reckoned on the same quantity of acetyl thiocyanate as before.

Assuming that acetylpiiperidylthiourea is first formed, a possible explanation of the production of piperidylthiourea is the following:

Two difficulties, however, stand in the way of its acceptance. The first is that, as a rule, trisubstituted thioureas are not very easily saponified, and therefore it is scarcely credible that cold alcohol should be able to remove the acetyl group; on the other hand, piperidylthiourea is formed with exceptional difficulty by the ordinary method,* and hence the acetyl derivative might conceivably present features differing from those of other compounds of this class. However, acetylpiiperidylthiourea can be prepared by the direct acetylation of this supposed piperidylthiourea, and its properties constitute the second difficulty as regards the suggested explanation.

On warming the supposed piperidylthiourea on the water-bath with excess of acetic anhydride, it soon dissolved, and crystals separated on

* The compiler has made several unsuccessful attempts to convert piperidine thiocyanate, by heating, into the isomeric thiourea.

cooling; when recrystallised from boiling water, they formed long prisms, easily distinguishable from the short, thick crystals of the parent substance, and melting at 112—113°. The new compound dissolves freely in alcohol or benzene; it is easily soluble in hot water, but sparingly in the cold solvent, and is nearly insoluble in light petroleum. Moreover, the acetyl group is very firmly held, for the solution was not desulphurised by ordinary treatment with alkaline salts of lead or silver, but yielded up its sulphur only after boiling with concentrated potassium hydroxide. A sulphur determination gave 17·3, the number calculated for $C_8H_{14}ON_2S$ being 17·21 per cent.

When boiled with alcohol, not a trace of ethyl acetate was formed; it is therefore certain that the piperidylthiourea resulting as described above does not originate through the action of alcohol on the acetyl-piperidylthiourea already formed.

(c) *Ammonia.*

In almost every case hitherto recorded where ammonia interacts with the thiocyanate of a fatty acid, little or no thiourea is formed, but the products of double decomposition, namely, thiocyanic acid, together with fatty amide appear instead. The first experiment of this kind was carried out by Miquel, who obtained from his acetyl thiocyanate an oil, miscible with water and having the empirical composition of acetamide thiocyanate; from this oil, a very small quantity of a crystalline solid was deposited, which he conjectured might possibly be acetylthiourea.

Since the power of acetyl thiocyanate to combine directly with aniline is so greatly enhanced at high temperatures, the question naturally arose whether this might also be favourable to its union with ammonia. In order to decide this point, ammonia gas (not dried) was led through a solution of the acetyl compound in boiling benzene; much fuming occurred, with separation of an oil which proved to be ammonium thiocyanate, and the liquor poured off from this deposited a small quantity of nearly pure acetylthiourea. On repeating the experiment with 8 grams of freshly distilled acetyl thiocyanate in boiling toluene, a little oil separated, which presently crystallised (ammonium thiocyanate); some hydrogen sulphide escaped, and from the residual liquor 2 grams of acetylthiourea were obtained, or a little more than 21 per cent. of the possible yield, supposing the acetyl compound to be purely thiocarbimide in function.

The above results, although not decisive, seem to point in the same direction as those obtained with aniline.

This concludes the work carried out by the author (R. E. D.) on acetyl thiocyanate.

PART II.

Carboxyphenyl- and Carboxyguaiacol-thiocarbamides.

The following preliminary experiments were carried out with the assistance of samples of the chlorocarbonates derived from phenol and from guaiacol, which had kindly been presented to the author by the Farbenfabriken vorm. F. Bayer & Co.

In order to prepare carboxyphenylthiocarbimide, phenyl chlorocarbonate, $C_6H_5O \cdot COCl$, dissolved in benzene, was left for some days in contact with finely powdered dry potassium thiocyanate until the solution ceased to give the reactions of chlorine; the solid was then removed at the pump and washed with more benzene. The filtrate had little pungent odour, and when shaken up with water afforded no thiocyanic acid, but gave with alkaline solutions of silver and lead salts the desulphurisation reactions indicating the presence of a thiocarbimide, and when treated with bases combined with them, evolving heat and producing the corresponding additive compounds.

Carboxyphenylmethylthiocarbamide, $C_6H_5 \cdot O \cdot CO \cdot NH \cdot CS \cdot NH \cdot CH_3$.

By mixing the benzene solution with aqueous methylamine, diluted with alcohol, and allowing the mixture to concentrate by evaporation, a somewhat oily solid was obtained, crystallising from alcohol, which dissolves it moderately easily when hot, but sparingly in the cold, in long, glistening prisms melting at $175-176^\circ$.

0.204 gave 0.228 $BaSO_4$. $S = 15.36$

$C_9H_{10}O_2N_2S$ requires $S = 15.27$ per cent.

This substance is isomeric with the carboxymethylphenylthiocarbamide, $MeO \cdot CO \cdot NH \cdot CS \cdot NHPh$ (m. p. 158°), obtained by the author (Trans., 1901, 79, 908) from carboxymethylthiocarbimide and aniline.

Carboxyphenylisoamylthiocarbamide, $C_6H_5 \cdot O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_5H_{11}$.

Using isoamylamine, a solid was obtained together with a good deal of oil, the latter being extracted at the pump: the crystalline solid, after washing with dilute alcohol, melted at $99-100^\circ$ and gave $S = 12.05$ against $S = 12.03$ per cent., calculated for $C_{13}H_{18}O_2N_2S$.

Carboxyisoamylphenylthiocarbamide, $C_5H_{11}O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$ (*loc. cit.*, p. 914), isomeric with the above compound, melts at $97-98^\circ$.

Carboxydiphenylthiocarbamide, $\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$.

Aniline gave the diphenylated derivative, which melted at $148-149^\circ$ and was easily desulphurised by alkaline lead tartrate.

Found, $\text{S} = 11.78$. $\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2\text{S}$ requires $\text{S} = 11.76$ per cent.

Acetylphenylthiocarbamide (2 grams), when warmed on the water-bath with excess of phenyl chlorocarbonate, gradually dissolved, whilst acetyl chloride escaped, and the resultant mixture, when cooled and treated with alcohol, yielded the above carboxydiphenyl compound (1.5 grams), melting at $148-149^\circ$:

Carboxyguaiacolphenylthiocarbamide,

This compound, like the preceding, was obtained by expelling the acetyl group from acetylphenylthiocarbamide, guaiacol chlorocarbonate being employed for the purpose. A solid was obtained, melting at $154-155^\circ$ and giving a fine mirror of galena when warmed with an alkaline solution of lead tartrate.

The composition was checked by means of a sulphur determination:

0.208 gave 0.159 gram BaSO_4 . $\text{S} = 10.5$.

$\text{C}_{15}\text{H}_{14}\text{O}_3\text{N}_2\text{S}$ requires $\text{S} = 10.59$ per cent.

By treating with alcoholic ammonia the solution containing the product of the action of phenyl chlorocarbonate on potassium thiocyanate, a solid was obtained melting at $169-170^\circ$; it was desulphurised at once in the cold by ammoniacal silver nitrate, and slowly on boiling with an alkaline lead solution. No analysis was made, but in view of the mode of preparation and the properties mentioned, there can be little doubt that this substance was carboxyphenylthiourea.

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